



UNIVERSITI PUTRA MALAYSIA

**CORRELATION OF SOME DIELECTRIC PROPERTIES WITH
PROCESSING AND MICROSTRUCTURE IN
Mg-Sn-O SYSTEM**

IFTETAN AHMAD TAHA

FSAS 1999 15

**CORRELATION OF SOME DIELECTRIC PROPERTIES WITH
PROCESSING AND MICROSTRUCTURE IN
Mg-Sn-O SYSTEM**

By

IFTETAN AHMAD TAHA

**Thesis Submitted in Fulfilment of the Requirements for the Degree of Master of
Science in the Faculty of Science and Environmental Studies,
Universiti Putra Malaysia**

February, 1999



**CORRELATION OF SOME DIELECTRIC PROPERTIES WITH
PROCESSING AND MICROSTRUCTURE IN
Mg-Sn-O SYSTEM**

IFTETAN AHMAD TAHA

**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

1999



To:

My Parents

Husband

And

Sisters.

ACKNOWLEDGEMENTS

Firstly, I am very grateful to “ ALLAH ” S.w.t. for giving me the strength, and patient, to complete this research within the specified time.

It is my pleasure to extend my sincere gratitude and indebtedness to Dr. Abdul-Majeed Azad for his continuous supervision, help, and fruitful discussion, without him this research will never be completed. Also I want to express my acknowledgement to my co-supervisor Associate Professor Dr. Abdul Halim Shaari, for his assistance and support during this research. I am also pleased to thank my co-supervisor Dr. Jamil Suradi for his encouragement and support.

I would also like to thank Dr. Mansor Hashim for his kind assistance, encouragement, support and providing the facilities used in this research which enable me to complete the research.

I would like to express my sincere gratitude to Mr. Saleh Al-Khawaldeh and Mrs. Noorhana Yahya for their assistance, discussion and moral support. I would like to thank all the undergraduate students in the materials science group for their friendly co-operation; also I want to thank all postgraduate students in the ferrite group and the superconductor group.

I want to thank Ms. Azilah Abdul Jalal (SEM unit, UPM) for her help during SEM analysis, special thank to Mr. Sri jegan (Chemistry Department, UPM) for his generosity and assistance.

Special thanks are due to my friend Mrs. Fars for her courage to continue this research with patient, and to all my Iraqi friends who encourage me to continue and complete my study.

My very special thanks goes to my family in Iraq, my father Prof. Ahmad Al-Haje Taha from Mosul University, Iraq, my mother for her praying for me and my kids, my lovely sisters and my brother in law for their support from far.

Finally, I want to thank my husband Dr. Waleed A. Thanoon for his generous support and assistance during my studies. Thanks to my kids Dalia, Kaldoon and Zadoon for the time they missed their mother.



TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	iii
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF PLATES	xv
LIST OF ABBREVIATIONS.....	xvi
ABSTRACT.....	xviii
ABSTRAK.....	xx
 CHAPTER	
 I INTRODUCTION	
Relevance/ Importance of Electronic Ceramics.....	1
General Introduction of Alkaline-Earth Stannates.....	4
The Objective of Work.....	6
 II LITERATURE REVIEW	8
Thermally Stable Capacitors.....	8
Magnesium Silicates and Magnesium Titanates	9
Mg ₂ SnO ₄ and Relevance	10
MSnO ₃ and Relevance.....	12
 III THEORY	16
Introduction.....	16
Perovskite Structure.....	17
Spinel Structure.....	18
Inverse Spinel	19
Polycrystalline Structure.....	21
Mixing and Milling.....	22
Compacting.....	23
Calcination	24
Sintering	26
Characterisation	28
Structural (Physical) Characterisation.....	30
X-ray Diffraction Analysis.....	30

	Qualitative Phase Analysis	32
	Quantitative Phase Analysis	33
	Microstructural Characterisation.....	34
	Scanning Electron Microscopy	35
	Impedance Spectroscopy.....	36
	Lumped Parameter/Complex Plane.....	39
	Bode Plot Analysis.....	47
	Ceramic Insulator and Capacitor Materials.....	47
	Dielectric Materials.....	48
	Dielectric Constant.....	48
	Dissipation Factor ($\tan \delta$).....	50
	Dielectric Breakdown Strength (K).....	50
	Temperature Coefficient of Capacitance.....	51
IV	METHODOLOGY.....	52
	Introduction.....	52
	Materials and Equipment.....	52
	Methods.....	53
	Solid –State Reaction (SSR) Route.....	53
	Self-Heat-Sustained Reaction (SHS) Route.....	59
	Characterisation Technique.....	60
	Microstructural Analysis.....	62
	Electrical Measurements	62
V	RESULT AND DISCUSSION.....	65
	Introduction.....	65
	Solid-State-Reaction (SSR) Derived Samples.....	66
	Structural Analysis.....	66
	Microstructural Analysis.....	71
	Electrical Analysis.....	78
	Self-Heat-Sustained (SHS) Derived Samples.....	97
	Structural Analysis.....	97
	Microstructural Analysis.....	98
	Electrical Analysis.....	105
	Temperature Coefficient of Capacitance (TCC) and Temperature Coefficient of Dielectric Constant (TCK)	122
VI	CONCLUSIONS AND SUGGESTIONS.....	131
	Conclusions	131

Suggestions.....	132
REFERENCES	134
APPENDICES	138
Appendix A.....	139
VITA	141



LIST OF TABLES

Table	Page
1 Cation Distribution in Unit Cell of Mg_2SnO_4	20
2 Calcination Temperatures and Duration Employed in This Work.....	56
3 Summary of TCC and TCK Values Computed from the Measurement Data on Sintered Mg_2SnO_4 Samples. For Comparison, those on the Related Systems are Also Listed.....	130

LIST OF FIGURES

Figure	Page
1. Electronic ceramic market.....	3
2. Pressure and temperature relationship phase diagram in MgO-SnO ₂ system (Jackson et al., 1974).....	13
3. Perovskite structure (Pumpuch, 1976).....	18
4. Spinel structure (Kingrey, 1979).....	19
5. Development of ceramics microstructure during sintering (a) loose powder particle (b) initial stage, (c) intermediate stage, (d) final stage (Lee, 1994).....	29
6. Derivation of Bragg's law for X-ray diffraction.....	31
7. Representation of a planer vector in orthogonal coordinate.....	32
8. Sample plots with associated simplified equivalent circuit for each of the four complex planes.....	39
9. Equivalent circuit for relaxation complex materials after voigt, maxwell and Ladder respectively.....	44
10. Representation of a significant conduction paths and corresponding equivalent circuit paths (McDonald, 1987).....	46
11. Flow chart for solid-state reaction route.....	58
12. Sintering schedule.....	60
13. Flow chart for self-heat-sustained reaction route.....	61
14. XRD patterns of SSR - derived powders on (1:1) molar ratio mixtures calcined at different temperature	67
15. XRD patterns for SSR and SHS in (1:1) molar ratio.....	68

16.	XRD patterns of powders in (2:1) molar mixtures obtained via SSR and SHS techniques after calcination at 1200 °C / 24 h.....	69
17.	XRD patterns of sintered pellets and powders obtained from SSR in (2:1) molar ratio mixture.....	70
18.	Morphological feature derived Mg_2SnO_4 via SSR technique: (a) milled powder; in 1:1 molar ratio (b) after calcined at 1100 °C / 12 h in 1:1 molar ratio; and (c) after calcination at 1200 °C / 24 h in 2:1 molar ratio.....	72
19.	Microstructural features of solid-state derived Mg_2SnO_4 sintered at 1200 °C: (a) for 24 h, surface; (b) for 24 h, fractured; (c) for 48 h, surface; (d) for 48 h, fractured.....	73
20.	Microstructural features of solid-state derived Mg_2SnO_4 sintered at 1300 °C: (a) for 12 h, surface; (b) for 12 h, fractured ; (c) for 24 h, surface; (d) for 24 h, fractured	75
21.	Microstructural features of solid - state derived Mg_2SnO_4 sintered at 1400 °C : (a) for 6 h, surface; (b) for 6 h, fractured and (c) for 12 h, surface	76
22.	Microstructural features of solid-state derived Mg_2SnO_4 sintered at 1500 °C: (a) for 2 h. surface; (b) for 2 h fractured; (c) for 6 h, surface and (d) for 24 h, fractured	77
23.	Microstructural features of solid - state derived Mg_2SnO_4 sintered at 1600 °C: (a) for 2 h, surface and (b) for 2 h, fractured	78
24 a.	Relaxation in and C^* plane for SSR sintered at 1500 °C/ 6 h.....	79
24 b.	Relaxation in and Z^* plane for SSR sintered at 1500 °C/ 6 h.....	80
25 a.	Relaxation in and C^* plane for SSR sintered at 1600 °C/ 2 h.....	81
25 b.	Relaxation in and Z^* plane for SSR sintered at 1600 °C/ 2 h.....	82
26 a.	Variation of capacitance for SSR samples sintered at 1400 °C / 6 h as a function of frequency at different temperatures in the range 27 °C to 300 °C.....	83
26 b.	Variation of capacitance for SSR samples sintered at 1400 °C /12 h as a function of frequency at different temperatures in the range 27 °C to 300 °C.....	84

26 c.	Variation of capacitance for SSR samples sintered at 1500 °C / 6 h as a function of frequency at different temperatures in the range 27 °C to 300 °C.....	85
26 d.	Variation of capacitance for SSR samples sintered at 1600 °C / 2 h as a function of frequency at different temperatures in the range 27 °C to 300 °C.....	86
27a.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at room temperature in samples sintered at °C / 6h.....	89
27 b.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 300 °C in samples sintered at 1400°C / 6h	90
28 a.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at room temperature in SSR samples sintered at 1500 °C / 6 h	91
28 b.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 200 °C in SSR samples sintered at 1500 °C / 6 h	92
28 c.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 300 °C in SSR samples sintered at 1500 °C / 6 h	93
29.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at room temperature in SSR samples sintered at 1600 °C / 2 h	94
30.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 200 °C in SSR samples sintered at 1600 °C / 2 h	95
31.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 300 °C in SSR samples sintered at 1600 °C / 2 h	96
32.	Morphological features of (a) calcined powder in 1:1 molar ratio at 1100 °C/ 12 h and (b) calcined powder in 2:1 molar ratio at 1200 °C / 24 h.....	99
33.	Microstructural features of self-heat-sustained derived Mg ₂ SnO ₄ sintered at 1200 °C : (a) for 24 h, surface; (b) f or 24 h, fractured; (c) for 48 h surface and (d) for 48 h fractured	100

34.	Microstructural features of solid-state derived Mg_2SnO_4 sintered at 1300 °C: (a) for 12 h, surface; (b) for 12 h, fractured; (c) for 24 h, surface and (d) for 24 h, fractured	101
35.	Microstructural features of self – heat – sustained derived Mg_2SnO_4 sintered at 1400 °C: (a) for 6 h, surface; (b) for 6 h, fractured; (c) for 12 h, surface and (d) for 12 h, fractured.....	102
36.	Microstructural features of self-heat-sustained derived Mg_2SnO_4 sintered at 1500 °C: (a) for 2 h, surface; (b) for 6 h, surface and (c) for 6 h, fractured..	103
37.	Microstructural features of self – heat – sustained derived Mg_2SnO_4 sintered at 1600 °C / 2 h: (a, b) 2:1 (surface & fractured) and (c, d) 1:1 (surface & fractured)	104
38a.	Relaxation in C^* plane for SHS sintered at 1500 °C/ 6 h.....	106
38b.	Relaxation in Z^* plane for SHS sintered at 1500 °C/ 6 h.....	107
39a.	Relaxation in C^* plane for SHS sintered at 1600 °C/ 2 h.....	108
39a.	Relaxation in Z^* plane for SHS sintered at 1600 °C/ 2 h.....	109
40a.	Variation of capacitance for SHS samples sintered at 1400 °C / 6 h as a function of frequency at different temperatures in the range 27 °C to 300 °C.....	112
40b.	Variation of capacitance for SHS samples sintered at 1500 °C / 6 h as a function of frequency at different temperatures in the range 27 °C to 300 °C.....	113
40c.	Variation of capacitance for SHS samples sintered at 1600 °C / 2 h as a function of frequency at different temperatures in the range 27 °C to 300 °C.....	114
41a	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at room temperature in samples sintered at 1400 °C / 6 h	115
41b.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 300 °C in samples sintered at 1400 °C / 6 h	116

42a.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 200 °C in samples sintered at 1500 °C / 6 h	117
42b.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 300 °C in samples sintered at 1500 °C / 6 h	118
43a	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at room temperature in samples sintered at 1600 °C / 2 h	119
43b.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 200 °C in samples sintered at 1600 °C / 2 h	120
43c.	Dependence of capacitance, dielectric constant and loss tangent on applied frequency at 300 °C in samples sintered at 1600 °C / 2 h	121
44a.	Variation of average capacitance and dielectric constant with temperature over a frequency range (10 kHz - 13 MHz) in SSR samples sintered at 1400 °C / 6 h.....	123
44b.	Variation of average capacitance and dielectric constant with temperature over a frequency range (10 kHz - 13 MHz) in SSR samples sintered at 1400 °C / 12 h.....	124
44c.	Variation of average capacitance and dielectric constant with temperature over a frequency range (10 kHz - 13 MHz) in SSR samples sintered at 1500 °C / 6 h.....	125
44d.	Variation of average capacitance and dielectric constant with temperature over a frequency range (10 kHz - 13 MHz) in SSR samples sintered at 1600 °C / 2 h.....	126
45a.	Variation of average capacitance and dielectric constant with temperature over a frequency range (10 kHz - 13 MHz) in SHS samples sintered at 1400 °C / 6 h.....	127
45b.	Variation of average capacitance and dielectric constant with temperature over a frequency range (10 kHz - 13 MHz) in SHS samples sintered at 1500 °C / 6 h.....	128
45c.	Variation of average capacitance and dielectric constant with temperature over a frequency range (10 kHz - 13 MHz) in SHS samples sintered at 1600 °C / 2 h.....	129

- 46. Concentration profile of Mg and Sn in Mg_2SnO_4 sintered at 1600 °C / 2 h. 139
- 47. Concentration profile of Mg and Sn in Mg_2SnO_4 sintered at 1500 °C / 26 h. 140

LIST OF PLATES

Plate		Page
1	10 mm Sample.....	55
2	Furnace.....	57
3	Scanning Electron Microscopy (SEM).....	57
4	Impedance Analyser.....	62

LIST OF ABBREVIATIONS

λ	Wave Length
a, b, c	Lattice parameters
d_{hkl}	Reciprocal d vector
hkl	Miller indices
XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
f, ω	Frequency and angular frequency
A	Cross Sectional Area
θ	Bragg angle
$\tan \delta$	Loss tangent
PVA	Polyvinyl alcohol
T	Temperature
TCC	Temperature Coefficient of Capacitance
TCK	Temperature Coefficient of Dielectric
K	Dielectric Constant
Cp	Capacitor
Gp	Conductor
logC	Logarithm of Capacitance
logf	Logarithm of Frequency
C	Capacitance
Tc	Critical Temperature

P	Pressure
t	Time
D	Diffusivity
$\beta_{1/2}$	Full width Half Maximum
I	Current
ϵ_o	Permittivity of Vacuum
V	Applied Voltage
EDAX	Energy Depressive Analysis by X-ray
Z	Impedance
M	Modulus
Y	Admittance
LP/CPA	Lumped Parameter /Complex Plane Analysis
α	Coefficient of Linear Thermal Expansion
ρ	Density
m	Mass
M ₂ S	Mg ₂ SnO ₄
MS	MgSnO ₃
AC	Alternating Current
ppm	Part per million

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

P	Pressure
t	Time
D	Diffusivity
$\beta_{1/2}$	Full width Half Maximum
I	Current
ϵ_o	Permittivity of Vacuum
V	Applied Voltage
EDAX	Energy Depressive Analysis by X-ray
Z	Impedance
M	Modulus
Y	Admittance
LP/CPA	Lumped Parameter /Complex Plane Analysis
α	Coefficient of Linear Thermal Expansion
ρ	Density
m	Mass
M ₂ S	Mg ₂ SnO ₄
MS	MgSnO ₃
AC	Alternating Current
ppm	Part per million

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

**CORRELATION OF SOME DIELECTRIC PROPERTIES WITH
PROCESSING AND MICROSTRUCTURE IN
Mg-Sn-O SYSTEM**

By

IFTETAN AHMAD TAHA

February 1999

Chairman: Abdul-Majeed Azad, Ph.D./ Mansor Hashim Ph.D.

Faculty: Science and Environmental Studies

The alkaline-earth stannates having the general chemical formula MSnO_3 ($\text{M} = \text{Ca}, \text{Sr}$ and Ba), have been projected as potential electronic ceramics (thermally stable capacitors, humidity sensor, carbon dioxide sensor, etc.). Even though magnesium is a member of the metal group to which Ca , Sr and Ba belong, no reliable technical information on the compounds in the pseudo-binary MgO-SnO_2 system appears to exist in the published literature. In view of the information gaps in the reported research, vigorous and systematic investigation has been carried out on the MgO-SnO_2 system.

The MgO-SnO_2 system has been thoroughly studied with respect to synthesis, processing and characterisation – physical, microstructural and electrical. Two different synthesis routes have been adopted. These routes are solid-state and self-heat-sustained. For each route two mixtures of different molar ratio viz., 2:1 and 1:1 have

been used. In 2:1 molar ratio mixtures Mg_2SnO_4 has been formed as a single phase upon calcination of starting materials at 1200 °C/ 24 h in both solid-state and self-heat-sustained techniques with one or two impurity peaks at 1200 °C/ 24 h. In 1:1 molar ratio, the reaction product consisted of a two-phase mixture of Mg_2SnO_4 and SnO_2 . Evaluation of microstructure that is intimately related to the envisaged properties in the ceramics has been closely and systematically followed as a function of sintering at different temperatures of (1200-1600 °C) and soak - time (2 - 48 h).

A thorough analysis of the as measured electrical data showed that the material possessed a very weak temperature dependence of capacitance (TCC) and dielectric constant (TCK) in the range 27-300 °C over several decades of frequency domain. It was found that TCC value varied between (-200 to +195) ppm / K thus holding the promise to its usage as a thermally stable capacitor component in high-speed electronic devices. The average dielectric constant was found to be in the range 10-18, thus identifying this material as a low dielectric constant system as well.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan ijazah Master Sains.

**KORELASI BEBERAPA SIFAT DIELEKTRIK DENGAN PEMROSESAN
DAN MIKROSTRUKTUR DALAM
SISTEM Mg-Sn-O**

Oleh

IFTETAN AHMAD TAHA

Februari 1999

Pengerusi : Abdul-Majeed Azad, Ph.D./ Mansor Hashim, Ph.D.

Fakulti : Sains dan Pengajian Alam Sekitar

Stanat alkali – bumi yang mempunyai formula kimia am $M\text{SnO}_3$ ($M = \text{Ca}, \text{Sr}$ dan Ba) telah diutarakan sebagai seramik elektronik yang berpotensi (kapasitor stabil terma, sensor kelembapan, sensor karbon dioksida dan sebagainya). Walaupun magnesium adalah dalam ahli kumpulan logam yang dipunyai oleh Ca , Sr dan Ba , tidak ada maklumat teknikal yang boleh dipercayai terhadap sebatian itu dalam sistem binari-pseudo MgO-SnO_2 yang wujud dalam penulisan yang diterbitkan. Memandangkan terdapatnya jurang maklumat dalam laporan penyelidikan, siasatan secara sistematik dan bersemangat telah dijalankan terhadap sistem MgO-SnO_2 .

Sistem MgO-SnO_2 ini telah dikaji secara menyeluruh terhadap sistesis, pemprosesan dan ciri-ciri fizikal, mikrostruktur dan elektrik. Dua laluan sintesis yang berbeza, iaitu teknik keadaan-pepejal dan tahan-haba-sendiri telah digunakan. Untuk kedua-dua laluan ini, dua campuran molar yang berbeza, dengan nisbah 2:1 dan 1:1 telah disediakan. Dalam campuran nisbah molar 2:1, Mg_2SnO_4 telah terbentuk sebagai fasa tunggal terhadap pemansan bahan awal pada suhu 1200°C / 24 jam dalam kedua-

dua teknik iaitu keadaan –pepejal dan tahan – haba – sendiri dengan satu atau dua puncak bendasing.

Dalam nisbah molar 1:1, produk tindakbalas terdiri daripada dua fasa campuran Mg_2SnO_4 dan SnO_2 . Penilaian terhadap mikrostruktur yang berkait rapat dengan sifat-sifat jangkaan dalam seramik telah diikuti rapat dan sistematik sebagai fungsi terhadap pensinteran pada suhu yang berbeza iaitu $1200 - 1600\text{ }^{\circ}\text{C}$ selama 2 – 48 jam.

Satu analisis yang terperinci terhadap data pengukuran elektrik menunjukkan bahawa bahan ini memiliki persandaran suhu yang amat lemah terhadap kapasitan (PSK) dan pemalar dielektrik (PSD) dalam julat $27 - 300\text{ }^{\circ}\text{C}$ untuk beberapa dekad domain frekuensi. Telah dijumpai juga bahawa nilai KPS berubah antara (-200 kepada +195) ppm / K dan sekaligus memberi jaminan kegunaannya sebagai komponen kapasitor stabil terma dalam peranti elektronik kelajuan – tinggi. Purata pemalar dielektrik yang telah dijumpai adalah dalam julat 10-18, justeru itu juga mengesahkan bahan ini sebagai sistem pemalar dielektrik yang rendah.

CHAPTER I

INTRODUCTION

Relevance / Importance of Electronic Ceramics

Ceramics materials are polycrystalline, inorganic materials which consist of metallic and nonmetallic elements bound together primarily by ionic and / or covalent bonds. The chemical composition of ceramic materials varies considerably, from simple compounds to mixtures of many complex phases bonded together. The earliest use of ceramics was in pottery and bricks (Koller, 1994).

The properties of ceramic materials also vary due to differences in bonding. In general, ceramic materials are typically hard and brittle with low toughness and ductility.

Ceramics are usually good electrical and thermal insulators due to the absence of conduction electrons. They have relatively high melting temperatures and high chemical stability in many hostile environments due to the stability of their strong bonds. In general, ceramics materials used for engineering applications can be divided into two groups: traditional ceramic materials, made